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COMMERCIAL PRODUCTION OF THYMOL FROM HORSEMINT (MONARDA PUNCTATA).

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INTRODUCTION.

It has long been known that thymol is present in considerable quantity in the oil distilled from horsemint (*Monarda punctata*), but so far as the writer had been able to learn no attempt has been made to cultivate this plant for the commercial production of thymol. In 1907 horsemint was observed to occur in abundance as a common weed on the sandy lands of central Florida, and the preliminary examinations of the oil from the wild plants which were made at that time seemed to indicate that a promising commercial source of thymol could be developed by bringing this plant under cultivation and selecting for propagation types of plants best suited for oil production.

The leaf area of the wild plants is rather small, and the herb when harvested consists mainly of woody stems which yield little or no oil. The fresh entire herb gathered in Putnam and Volusia Counties, Fla., yielded from 0.12 to 0.20 per cent of oil, although in some samples the yield fell far below these figures, owing to the excessive proportion of stems. The content of total phenols in these oils ranged from 56 to 62 per cent, and it was found that the phenols consisted almost entirely of thymol.

The first problem, therefore, seemed to be to increase the leaf area and thus increase the yield of oil per acre. Accordingly, in 1910 a small plat of ground was set with plants grown from a mixed collection of seeds secured from wild plants in Volusia County. Of the first year's growth from this plat, 196 pounds of herb was distilled and yielded 0.17 per cent of oil. In the second year the yield of oil from plants grown on the same plat was 0.24 per cent. The content of total phenols in the oils was found to be 64 per cent.

A large number of variations in the plants were noted in 1910, and from these about sixty individual plants showing the various forms were selected for seed purposes. The seed from these plants was sown in 1911, but the resulting plants were not true to type. It was noted, however, that the variations fell into two general classes—dark and light plants—and that to a large extent these variations came true to type. The dark plants had much darker leaves, more serrate, and with a pronounced red color in the stems and branches. The light plants had larger leaves, lighter green in color, and with little or no red color in the stems and branches. There was also a greater tendency to the production of leaves in the light than in the dark type. From 34 tests which were made to show the relative yield of oil of these two types of plants the following average yields of oil were obtained: From the dark type, 0.40 per cent of oil, which contained 66 per cent of phenols; from the light type, 0.42 per cent of oil, with 69 per cent of phenols. The specific gravity, as well as the percentages of oil and of phenols in the oil, was found to be higher in the plants of the light type. Future seed selection was therefore carried on with this type.

In 1912 a further comparison was made between the light and dark forms and the results obtained were still more marked, but owing to weather conditions all samples showed a low yield of oil. The average of 36 tests was as follows: Dark type, 0.31 per cent of oil, which contained 65 per cent of phenols; light type, 0.40 per cent of oil, which contained 68 per cent of phenols. By continuing the selection of the light type of plants the yield of oil has been gradually increased, and in 1914 the herb from a plat of two-thirds of an acre yielded 0.44 per cent of oil, which contained 72 per cent of phenols, while in 1915 the average was 0.42 per cent of oil, containing 74 per cent of phenols.

During these years selection was also made to increase the size of the plants in order that the tonnage of herb per acre might be increased. This was also successful and a considerably increased yield was noted year by year. It is believed that at the present time the selection has been carried far enough to warrant the use of the improved form for the commercial production of thymol in the United States.[1]

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[1] The department has no supply of selected seed or plants of horsemint available for distribution.

CULTURAL METHODS FOR HORSEMINT.

PLANTING THE SEED.

The seed of horsemint matures in the Southeastern States during August and September and is ready to be gathered as soon as the calyx is dry and has assumed a dark-brown color. If left too long the largest and best seed will be lost and only the inferior seed will remain for collection. The seed can readily be gathered by hand by stripping off the entire heads, together with such leaves or bracts as remain on the stem. This material should be spread on a cloth or tight floor and as soon as it is thoroughly dry the seeds can be removed by rubbing through a sieve having 12 to 16 meshes to the inch, common window screening being about the right size. Further sifting and very gentle winnowing will remove most of the foreign material.

In the extreme Southeastern States, where the winters are free from severe frosts and snow, the best results are secured by planting the seed about the first of November in a carefully prepared seed bed. In order to avoid too thick sowing it is advisable to mix the seed with dry sand and sow the mixture evenly on the seed bed. A bed of 15 square feet will provide enough plants for an acre if properly planted.

After the seed has been sown, a layer of fine soil about one-eighth of an inch thick should be sifted over it and the bed well shaded by cloth. A good form of seed bed is that used by market gardeners in the South for raising celery plants. The soil should be kept moist, and as soon as the plants begin to come up the cloth should be removed. The seed will germinate in from six to ten days, and at two months from sowing the plants should be 2 inches high and ready for transplanting to the fields. If this work is done following a rain and the soil is in good condition no watering is necessary.

SOILS.

Horsemint occurs wild on light sandy soils and under cultivation has given the best results on this type of soil. It is essentially a lime-loving plant and its culture has not been successful on soils which were strongly acid, nor on heavy clays or low land where the drainage was poor or the amount of moisture excessive. The best results have been secured on rich, well-drained sandy loam, underlain with marl or clay at a depth of from 2 to 3 feet. Considering all the factors involved in the commercial production of this plant, it probably would be advisable to make plantings on light sands, such as the high pine lands of the Southeastern States. Horsemint occasionally occurs wild in dry fields on sandy soils from southern New York to Florida and westward to Wisconsin, Kansas, and Texas. It probably would thrive under cultivation wherever it is found growing wild, although its profitable production will depend upon local economic conditions.

CULTIVATION AND FERTILIZERS.

The plants should be set in the field in rows 3 feet apart and about 18 inches to 2 feet apart in the row. This will permit the use of horse cultivation as soon as the plants have become established in the field. The usual cultivation should be given until the plants are large enough to shade the ground and thus prevent the growth of weeds which might injure the crop at harvest time.

In 1912 a series of fertilizer experiments was carried out on 36 plats. It was found that although certain special methods of treatment had a marked effect on the percentage of yield of oil and of thymol in the oil, the greatest yield was obtained by promoting the growth of the plant and thus securing the largest possible yield of herb per acre.

Acid phosphate gave more herb and a higher percentage of oil than did bone black, and calculated on the yield of thymol per acre the ratio was as 2 to 1 in favor of the acid phosphate. Nitrate of soda did not give as satisfactory results as sulphate of ammonia. The use of an organic source of nitrogen in the complete formula did not give as good results as when all the nitrogen was applied in the form of sulphate of ammonia. There was a slight difference in favor of the application of the potash in the form of sulphate. The best results were obtained by the use of a complete fertilizer having the following analysis: Nitrogen, 4 per cent; phosphoric acid, 6 per cent; potash, 10 per cent. With this fertilizer made from sulphate of ammonia, acid phosphate, and sulphate of potash, 600 pounds per acre should be sufficient to produce a good crop, and less could be used on land having a fair degree of fertility.

It has been found advisable to make the application of fertilizer after the plants have become established in the field, but care should be taken to prevent injury to the leaves by the fertilizer.

The average composition of a number of samples of horsemint made both before and after distillation is shown in Table I, the results being calculated on the basis of dry material.

TABLE I.—*Composition of horsemint before and after distillation.*

Time of analysis.	Ash.	Nitrogen, as ammonia.	Phosphoric acid, as P_2O_5.	Potash, as K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Before distillation	7.73	1.46	0.58	2.38
After distillation	8.17	1.33	.54	2.12

Taking as a basis the average composition of the herb before distillation and allowing 25 per cent as the average quantity of dry matter, the quantity found in a large number of determinations, it appears that a crop of 10,000 pounds will remove from one acre of land the following quantities of nutrient materials: Nitrogen, as ammonia, 38.5 pounds; phosphoric acid, as P_2O_5, 14.5 pounds; and potash, as K_2O, 59.5 pounds. The materials removed from the soil could be replaced by the use of 800 pounds per acre of fertilizer having the following composition: Nitrogen, as ammonia, 4.81 per cent; phosphoric acid, as P_2O_5, 1.81 per cent; and potash, as K_2O, 7.43 per cent.

Since some disposal must be made of the distilled herb it is probable that this material if returned to the soil would restore most of the nutrient materials removed and at the same time add vegetable matter to the land. It is advisable, however, to compost this material and to apply it to the field only after it is well decomposed. The exhausted material has been found to contain an average of 50 per cent of water; and if proper allowance is made for the water content a ton of this material would yield the following quantities of nutrient materials: Nitrogen, as ammonia, 13.3 pounds; phosphoric acid, as P_2O_5, 5.4 pounds; and potash, as K_2O, 21.2 pounds.

HARVESTING.

In harvesting the crop excellent results were secured by the use of a 1-horse mowing machine, which was made adaptable for the purpose by placing shoes under each end of the cutting bar, so that the plants were cut about 6 inches above the ground. As soon as it is cut the herb should be gathered and hauled to the distilling plant, since it has been found that by allowing the plants to dry in the field there is considerable loss of oil. A large loss of leaves also results, owing to their rapid drying and shattering off in handling. Care must be taken in harvesting that the rooted layers about the plant are not torn loose; otherwise, a large percentage of the plants left in the field will die. The lower branches of the plant which spring from the stems near its base grow downward and strike root by natural layerage, and since in a large number of cases the old root dies after the first year the plant is perpetuated by these layers. In light soils these roots are easily torn loose and the death of the plant results. On this account the use of a rake for getting up the cut herb is undesirable, and forks should be used for that purpose.

Considerable work, extending over a period of several years, has been done in order to determine the proper time for harvesting the herb and also to ascertain the yield of oil and thymol at the different stages of growth. In 1911, 16 tests were made with plants in the budded stage and a like number with plants in full flower, to determine the percentage of yield of oil and thymol in these two stages. The average yield was as follows: In the budded stage, 0.36 per cent of oil, with 64 per cent of total phenols; from the plants in full flower, 0.33 per cent, with 67 per cent of phenols. In order to gather further data on this point tests were made in 1912 with plants in various stages of growth harvested from measured areas. The results obtained are summarized in Table II, which also shows the same results reduced to the basis of yield per acre.

TABLE II.—*Yield of oil and total phenols from horsemint at different stages of growth.*

Stage of growth.	Weight of herb distilled.	Actual yield.		Yield per acre.		
		Oil.	Total phenols.	Herb.	Oil.	Phenols.
	Pounds.	*Per cent.*	*Per cent.*	*Pounds.*	*Pounds.*	*Pounds.*
Plants just beginning to send up flower stalks	453	0.34	72	9,690	32.94	23.05
Budded stage	506	.30	76	10,590	31.77	24.14
Full flower	1,403	.24	74	10,000	24	18.48
Flowers fallen	352	.18	74	8,500	15.30	10.82

From these results it will be seen that the highest yield of phenols is secured in the budded stage and that the loss is very rapid as the flowering period advances. Since, however, the difference is but slight between the first and second stages, it is advisable with a large acreage to begin harvesting about the time the flower stalks begin to shoot up; otherwise, it may not be possible to harvest part of the area until the flowering stage is well advanced, and thus loss will result.

DISTILLATION.

Distillation of the horsemint herb is carried on by the usual methods in practice for distilling such volatile oils as peppermint and spearmint. A retort made of wood, galvanized iron, or boiler iron is used to contain the herb. This retort is connected to a condenser by a pipe of proper size from the top of the retort. The condenser may be of the worm type, such as is used in the distillation of turpentine, or of the tubular type, with flues similar in arrangement to a vertical boiler. Steam from a boiler is admitted to the retort at the bottom and passing through the herb enters the condenser, where the mixed vapors of steam and oil are cooled by a water jacket. The mixture of water and oil flowing from the condenser should be collected in a receptacle having a side tube entering the container at the bottom and bent up so that the outlet is only about 2 inches below the top of the container. This will allow the water to be discharged through the side tube, while the oil is retained as a layer on top. It has been found advisable to retain the water which flows from the oil receiver, in order to recover the oil dissolved in it, since this recovered oil is very rich in thymol.

In 1911, 4 gallons of this water was allowed to stand for several days until it was perfectly clear and all the oil globules were removed. When redistilled a yield of 0.114 per cent of oil was secured, containing

95 per cent of total phenols. In 1912 a total of about 35 gallons of water was distilled and a yield of 0.05 per cent of oil was secured, having 98 per cent of phenols. The quantity of oil which is dissolved in the water under the usual methods of distillation is strikingly shown by the results for 1914, which are summarized in Table III.

TABLE III.—*Quantity of oil recovered from the water as compared with that obtained from horsemint.*

Weight of herb.	Oil from the herb.	Oil recovered from the water.
	Pounds.	*Pounds.*
441 pounds	1.6	0.20
395 pounds	1.8	.19
302 pounds	1.2	.12

For the year 1914 the oil recovered from the water contained 90 per cent of phenols.

From these results it will be seen that the redistillation of this water is practicable and will add about one-seventh to the quantity of oil secured from the herb. This redistillation can readily be accomplished by collecting the water in a suitable receptacle, and when a sufficient quantity has accumulated it can be run into the retort and distilled in the same manner as the herb, or the water secured can each time be added to the next charge of herb and distilled with it.

By passing the fresh herb through a fodder cutter or shredder it is possible to distill a larger quantity at a time, but it in no way hastens the distillation process; on the contrary, it hinders somewhat the unloading of the material if it is removed from the top of the retort. If the retort is emptied from the bottom, as is customary in the larger distillation plants, it is practicable to cut the herb, since it much facilitates the dumping. These are points which the distiller must decide according to his special conditions and the scale of his operations.

The size and number of the retorts used will depend upon the quantity of material to be distilled during the season. If the herb is cut before distillation, about 100 pounds can be contained in each 7 cubic feet of retort space. A retort 6 feet in diameter and 8 feet high would contain about 3,200 pounds of the cut herb, or about half that quantity of the whole herb.

As soon as it is distilled the oil should be freed from water in a separatory funnel and shaken with a small quantity of anhydrous calcium chlorid to remove the last traces of water and to prevent turbidity. It can then be stored until wanted for refining. It is preferable to use glass containers if the oil is to be stored for any length of time, since contact with iron or tin will darken the oil and make the refining more difficult.

EXTRACTION OF THE THYMOL.

The oil of horsemint distilled from plants grown in Florida consists of phenols to the extent of 70 to 80 per cent, and these phenols consist almost entirely of thymol, there being present also very small quantities of carvacrol. The nonphenol portion of the oil consists largely of cymene, which acts as a solvent for the thymol and prevents complete crystallization. It is therefore necessary to separate these two compounds as a preliminary step in the extraction of the thymol.

Since the two main constituents have a widely different boiling point, cymene boiling at 175° to 176° C. and thymol at 232° C. under normal pressure, almost complete separation can be secured by fractional distillation. The method devised for the separation is as follows: The crude oil is distilled in a proper retort of copper, which is fitted with an efficient fractionation column, the one used in these experiments with the best results being the Hempel form. Distillation is carried on slowly and the portion of the oil coming over below 215° C. is set aside. The temperature is then raised slightly and the fraction distilling over between 215° and 240° C. is secured. The residue in the retort is a thick, tarlike mass and so far as known is of no value.

Practically all the thymol is now contained in the second fraction, which consists of a rather heavy, slightly yellow liquid. The quantity of thymol contained in the first fraction should not be large if the process has been carried on carefully, but may run as high as 25 to 30 per cent. This fraction is now redistilled under the same conditions as before, and the second fraction secured between 215° and 240° C. is placed with the first one secured at this temperature and the residue discarded.

The total fractions secured between 215° and 240° C. are allowed to cool in a shallow container and a small crystal of thymol is added to start crystallization. Within a few minutes a heavy crop of crystals will be secured. After standing over night the crystals are separated from the mother liquor by means of a centrifuge, and the crystals are washed with water while the centrifuge is running at full speed and then dried by continued running of the centrifuge for three to five minutes.

If cooled in a freezing mixture or by setting in a cold place, the mother liquor will deposit another crop of crystals, but if a very large quantity of mother liquor is present it indicates that a considerable portion of the lower boiling fractions was not removed. It should, therefore, again be distilled in the same manner as before and the fraction secured between 215° and 240° C. should be treated in the manner previously described.

A sample of 28 pounds of horsemint oil, showing on assay 72 per cent of total phenols, was worked up by this process and 18 pounds of pure thymol was manufactured from it, which is equal to a commercial yield of 64.3 per cent of thymol from the oil. When made by this process a perfectly white crystalline product was secured; 15 pounds of thymol made by this process in 1915 was sold to the trade at a high price. Should a slightly yellow product be secured a second distillation would be required. It has been found, however, that with ordinary care a high-grade product will result from the first distillation. By this process three residues are secured in small quantities, the lower boiling fraction consisting largely of cymene, the mother liquor from the last crystallization of phenols, and the tarlike residue remaining in the retort after the last fraction has been removed. Work is at present under way looking to the utilization of these residues.

In order to provide an inexpensive and practical apparatus for the extraction of thymol from the oil on a moderate scale, the following apparatus has been devised:

(1) A flask 12 inches in diameter and 16 inches high, made of about 30-ounce copper. The top is brought to a short neck 3 inches in diameter and reenforced by a brass band half an inch wide and one-quarter inch thick, turned edgewise to form a ring and brazed to the neck, forming a flange. The seam in the flask must be brazed, since the temperature of the boiling oil is above the melting point of solder.

(2) A column 22 inches long of 3-inch thin-walled brass or copper tubing. The lower end is fitted with a brass ring of the same size and in the same manner as the neck of the flask and with it forming a flange joint. In the lower end of the column is brazed a brass or copper disk, set at an angle of about 30°. The top of the tube is covered with a cap, brazed on, and in the center is set a piece of three-fourths inch brass tubing, about 1 inch long, forming a neck, into which a cork can be fitted. About 4 inches below the top a side tube of 1-inch brass tubing is brazed in a slight angle downward. This tube should be about 20 inches long and at the free end should have an elbow which just fits into the end of the condenser.

The condenser is of copper, 4½ inches in diameter and about 20 inches long, and consists of an outer cylinder with a head at each end. Running through from one head to the other are seven quarter-inch tubes of copper or block tin. A side tube at the bottom and one at the top serve for the inlet and outlet of the cooling water, which moves from the bottom upward about the flues. To each end is soldered a brass collar 2 by 2 inches, which serves as a chamber about the ends of the flues. This slips over the enlarged end of the delivery tube at the top to form a fairly tight joint, while over the bottom collar is placed a funnel-shaped nozzle to collect and deliver as one stream the liquids which run down the flues. The entire condenser can be made with soldered joints, since the water jacket will prevent melting. A complete condenser can be bought from dealers in chemical and pharmaceutical apparatus or can be made at small expense by any good coppersmith.

The apparatus should be set up with the flask supported over a good flame which can be easily regulated, such as that from a large oil burner or from a gas or gasoline burner. The condenser is supported in a vertical position and the bottom side tube connected with a supply of cold water. The column is filled to within 1 or 2 inches of the side tube with glass beads one-half inch in diameter or with small unpainted baked clay or glass marbles. The hole in the top of the column is fitted with a tight cork, through the center of which a tube is placed just large enough to admit a common chemical thermometer graduated in centigrade degrees, with the scale reading from 100 to 300. This thermometer should be placed through the cork so that the bulb is just opposite the side tube. The flask is then filled a little more than half full of the horsemint oil and the joint between the flask and the column made tight with a leather gasket and clamp, or it may be secured by the use of a ground-joint brass union, one half of which is brazed to the neck of the flask and the other half to the column. This does away with the use of the gasket, which must be frequently renewed.

An apparatus of the size described will take 15 pounds of oil at a charge and in a day work up 75 to 100 pounds of oil. The cost of construction would be about $50.

YIELD PER ACRE.

During the past five years areas up to 1 acre in extent have been grown on various soils and as far as possible under actual commercial conditions. The results thus far secured show that an average of 20 pounds of oil per acre from first-year plantings may be regarded as a fair crop, although the test areas have sometimes shown a greater quantity. In succeeding years the yield should be at least 30 pounds of oil per acre, and under good conditions 40 pounds may be expected. Assuming the average phenol content of the oil to be 70 per cent, a figure which is somewhat below the average found for five years, and using the process of manufacture previously described, there may be expected for the first year a yield of 12.86 pounds of pure thymol per acre and for the succeeding years, 19.29 pounds per acre. Taking $2 per pound as the average price of thymol for a period of years, there would be a gross return per acre the first year of $25.72 and for each succeeding year, $38.58. In addition to this there should doubtless be added a small amount for the value of the residues, which at the present time has not been determined.

COMMERCIAL PROSPECTS.

For many years the commercial source of thymol has been chiefly the oil of *Carum ajowan* derived from ajowan seed, which is grown in the region of northern India and shipped to northern Europe, where the thymol is extracted. Thymol is extensively used in medicine and serves as an antiseptic. It is used internally for the treatment of certain conditions and is the basis of a number of important pharmaceutical compounds.

The importation of thymol for the 10 years 1906 to 1915, inclusive, as compiled from the weekly report of "Imports for consumption" in the Oil, Paint, and Drug Reporter, is shown in Table IV.

TABLE IV.—*Importation of thymol for 10 years, 1906 to 1915, inclusive.*

Year.	Imports.	Year.	Imports.
	Pounds.		*Pounds.*
1906	2,983	1911	3,576
1907	4,753	1912	2,930
1908	5,010	1913	6,620
1909	10,336	1914	18,048
1910	3,352	1915	2,031

From these figures it would seem that the annual consumption of thymol in the United States is sufficiently great to warrant a small industry for its production when carried on in connection with the distillation of other volatile oils.

The estimates of the cost of production summarized in Table V are based on the conditions existing in central Florida, where actual field tests have been made for several years. Such items as land rent, taxes, etc., are not included, nor has any allowance been made for depreciation, upkeep, or interest on the distilling plant, since it is doubtful whether the profits are sufficient to warrant the starting of an independent industry in thymol production if all the costs of equipment for the year are to be charged to this item alone.

TABLE V.—*Estimates of cost per acre for producing horsemint.*

Expenses.	First year.	Each succeeding year.
Growing plants in seed bed	$1	....
Fitting land	3	....
Planting in field	3	....
Fertilizer	8	8
Cultivation	2	1
Harvesting and distilling	6	10
Total	23	19

In these estimates it has been assumed that the residues on removing the thymol from the oil will at least pay the cost of manufacture. It has been determined that a plantation of horsemint will not need to be replanted oftener than once in five years, and under average soil conditions it is possible that it will continue to give a full yield for a still longer time. Consideration should also be given to the fact that after the first year a material reduction can be made in the cost for fertilizers if the distilled herb after being well decomposed is returned to the soil, since, as has been previously stated, this will restore much of the nutrient materials removed by the crop. The estimated returns show that a profit of about $16 per acre may be expected as an average for a 5-year period.

It has been shown that horsemint can be grown on the lighter types of soil at comparatively little expense, and as the cost of transportation for the finished product, thymol, is very low, it would seem that the production of this crop might be profitable when grown in connection with other oil-yielding plants for which a distilling apparatus is required.

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